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Two-Electron, One- and Two-Center Integrals

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IN a recent note,[1] Prosser and Blanchard mentioned the use of the Fourier convolution theorem method for the evaluation of one-electron, two-center integrals. This method has been applied by the author to one-electron integrals involving nonintegral Slater orbitals[2] and to one-electron integrals involving solid spherical harmonic operators.[3]

The present note is concerned with the application of this method to the evaluation of two-electron, two-center integrals[4] (see Fig. 1) of the type

$$I=\int f(\mathbf{r}_{a1})g(\mathbf{r}_{b2})h(\mathbf{r}_{12})d\mathbf{r}_1 d\mathbf{r}_2. \tag{1}$$

The integral is recovered by

$$I=(2\pi)^{-3}\int \bar{f}(\mathbf{k})\bar{g}(\mathbf{k})\bar{h}(\mathbf{k})\exp(-i\mathbf{k}\cdot\mathbf{R})d\mathbf{k}, \tag{2}$$

where the bar indicates the appropriate Fourier transform

$$\bar{\phi}(\mathbf{k})=\int \exp(i\mathbf{k}\cdot\mathbf{r})\phi(\mathbf{r})d\mathbf{r}. \tag{3}$$

In the corresponding one-center case (the limit as $\mathbf{R}$ goes to zero), the centers a and b coalesce (so that the subscripts a and b can be dropped) giving rise to the integral

$$J=\int f(\mathbf{r}_1)g(\mathbf{r}_2)h(\mathbf{r}_{12})d\mathbf{r}_1 d\mathbf{r}_2, \tag{4}$$

which is recovered by

$$J=(2\pi)^{-3}\int \bar{f}(\mathbf{k})\bar{g}(\mathbf{k})\bar{h}(\mathbf{k})d\mathbf{k}. \tag{5}$$

As an example of Eqs. (4) and (5), Pitzer and Hameka[5] have discussed the one-center integral

$$J=(32\pi)^{-2}\int r_1^4\cos^2\theta_1 r_2^4\cos^2\theta_2(r_{12}^{-3}-3z_{12}^2r_{12}^{-5})$$
$$\times\exp(-r_1-r_2)\sin\theta_1\sin\theta_2 dr_1 dr_2 d\theta_1 d\theta_2 d\phi_1 d\phi_2. \tag{6}$$

The transform[6] of $f(\mathbf{r}_1)=r_1^2\cos^2\theta_1\exp(-r_1)$ is given by

$$\bar{f}(\mathbf{k})=32\pi(1+k^2)^{-4}[1-k^2-4k^2P_2(\cos u)]. \tag{7}$$

Since the function $g(\mathbf{r}_2)$ is identical, its transform is also given by Eq. (7). For the transform of

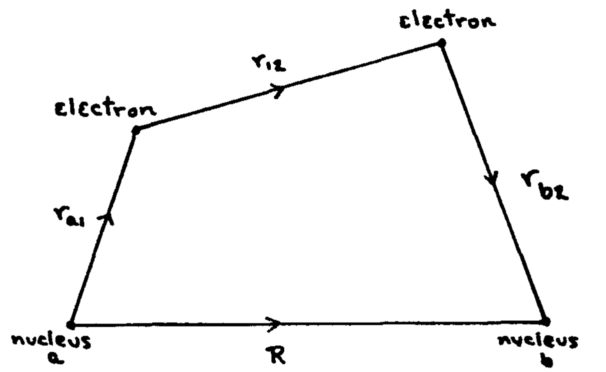

FIG. 1. Coordinate system.

$$h(\mathbf{r}_{12})=r_{12}^{-3}-3z_{12}^2r_{12}^{-5}=-2P_2(\cos\theta_{12})/r_{12}^3, \tag{8}$$

we have

$$\bar{h}(\mathbf{k})=8\pi P_2(\cos u)/3. \tag{9}$$

After substituting Eqs. (7) and (9) into Eq. (5), and integrating over u and v (the angular components of the k vector), we find

$$J=\frac{32\pi}{105}\left[11\int_0^\infty\frac{k^6}{(1+k^2)^8}dk-7\int_0^\infty\frac{k^4}{(1+k^2)^8}dk\right]. \tag{10}$$

When these two simple integrals of Eq. (10) are evaluated, the result $J=-\frac{1}{1680}$ is obtained in agreement with the result quoted by Pitzer and Hameka.[5]

An interesting point to notice is that this method does not involve the introduction of delta-function terms. The method is further not limited to one-center nor to specific forms for the f, g, and h functions.

The author wishes to acknowledge the informative discussions with Dr. Howard B. Levine of North American Aviation Science Center as to the range of validity of the Fourier convolution theorem.

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[5] R. M. Pitzer and H. F. Hameka, J. Chem. Phys. **37,** 2725 (1962).
[6] See Ref. 3 for the method of evaluation of the transforms in detail.